Synthesis of New Polymeric Antioxidants

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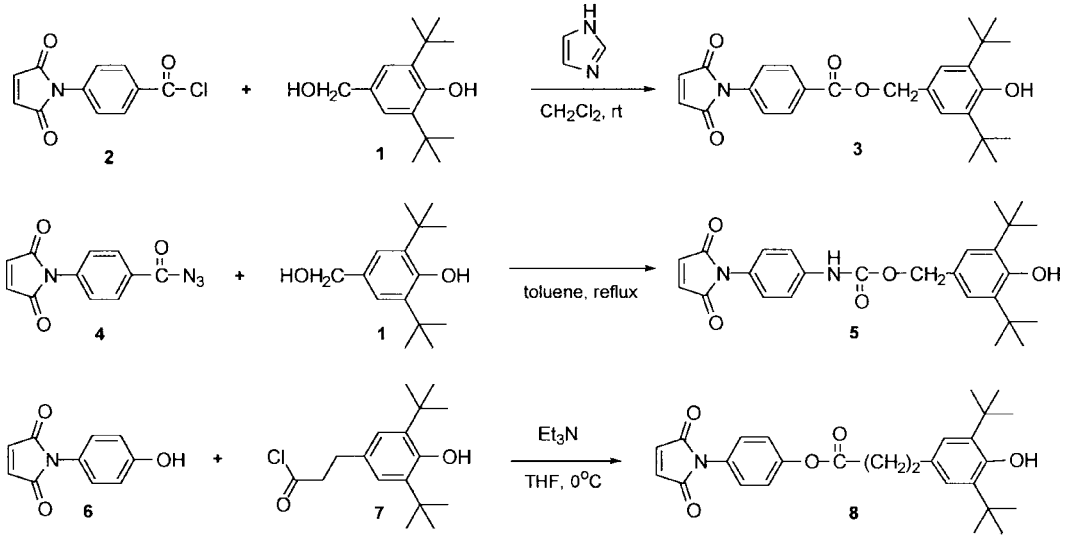
Polyolefins are very susceptible to thermal oxidative degradation. Oxidation reactions are enhanced at elevated temperatures during the processing of the polymer. The addition of antioxidants is the most convenient and effective way to block the thermal oxidation of polyolefins. Hindered phenol antioxidants, which contain the 2,6-di-*tert*-butylphenol functional group, are very effective primary antioxidants.[1,2] However, low molecular weight antioxidants are easily lost from the polymers by the physical loss such as migration, evaporation, and extraction. Physical loss of antioxidants therefore constitutes a major concern in the environmental issues and safety regulation, as well as in long-term use of polymers. Thus far, polymeric antioxidants have gained much interest to overcome the physical loss of antioxidants and to enhance the thermal stability.[3-5] The copolymerization or homopolymerization of the monomeric antioxidants is a conventional methodology for preparing polymeric antioxidants. Therefore the preparation of functional monomer containing hindered phenol is very important first step. Several monomeric antioxidants have been reported, many of them are based on the derivatives of acrylate.[5] In this paper, we report the synthesis of new polymeric hindered phenol antioxidants containing a maleimide as a polymerizable functionality (Scheme 1).

Experimental Section

General. The reagent grade chemicals were purchased from Aldrich Co. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. All solvents were reagent grade. Anhydrous solvents were dried immediately before use. Dichloromethane (DCM) was purified by drying with phosphorus pentoxide, followed by distillation. Tetrahydrofuran (THF) and toluene were distillated from sodium bezophenone ketyl.

^{1}H NMR spectra were recorded on 300 MHz spectrometer; chemical shifts are reported in ppm using TMS as internal standard. IR spectra were recorded on Nicolet FT IR spectrometer. Elemental analyses were performed at the Korea Basic Science Institute, Seoul, Korea. Melting points were determined on a capillary apparatus and uncorrected. Analytical TLC was performed on 0.25 mm precoated silica gel plates. Flash column chromatography was carried out with 230-400 mesh silica gel.

Synthesis of Monomeric Antioxidant 3. To a solution of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (1 g, 4.23 mmol) **1**[6] and imidazole (0.32 g, 4.7 mmol) in dry DCM (20 mL) was added a solution of *N*-[4-(chlorocarbonyl)phenyl]male-



Scheme 1

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imide **2**[7] (1.00 g, 4.24 mmol) in dry DCM (30 mL). The reaction mixture was stirred for 3 h, poured into water, extracted with ether, dried, filtered, and evaporated. The crude product was purified by flash column chromatography to give the desired monomeric antioxidant in 60% yield. R_f = 0.4 (ethyl acetate/hexane, 3 : 7); mp 185-188 °C; ^{1}H NMR ($CDCl_3$) 8.17 (2H, d, Ar), 7.49 (2H, d, Ar), 7.26 (2H, s, Ar), 6.87 (2H, s, vinyl), 5.29 (1H, s, OH), 5.28 (2H, s, CH_2), 1.46 (18H, s, CH_3); IR ($CDCl_3$, cm^{-1}) 3524, 2954, 1716. Anal. Calcd for $C_{26}H_{29}NO_5$: C, 71.69; H, 6.72; N, 3.22. Found: C, 71.37; H, 7.16; N, 3.36.

Synthesis of *N*-[4-(Azidocarbonyl)phenyl]maleimide 4. To a solution of compound **2** (1 g, 4.24 mmol) in DCM (15 mL) was added dropwise with syringe a solution of sodium azide (0.31 g, 4.67 mmol) in water (5 mL) and a phase transfer catalyst of triethylamine (0.15 mL, 1.48 mmol) and HCl (0.1 mL, 1.48 mmol) in water (5 mL) at room temperature. The reaction mixture was stirred for 30 min at room temperature, washed with water (15 mL × 3), and dried, filtered, and evaporated. The crude product was purified by flash column chromatography to give the desired compound **4** in 95 % yield. R_f = 0.5 (DCM); mp 137-138 °C (lit.[9] 120-121 °C); ^{1}H NMR ($CDCl_3$) 8.25-8.20 (2H, m, Ar), 7.67-7.63 (2H, m, Ar), 6.93 (2H, s, vinyl).

Synthesis of Monomeric Antioxidant 5. To a solution of maleimide **4**[7] (1 g, 4.13 mmol) in dry toluene (20 mL) was added a solution of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol **1** (0.98 g, 4.15 mmol) in dry toluene (30 mL). The reaction mixture was stirred for 3 h in condition of reflux, cooled to room temperature, and evaporated. The crude product was purified by flash column chromatography to give the desired monomeric antioxidant in 80% yield. R_f = 0.4 (ethyl acetate/hexane, 3 : 7); mp 164-165 °C; ^{1}H NMR ($CDCl_3$) 7.50 (2H, d, Ar), 7.29 (2H, d, Ar), 7.26 (2H, s, Ar), 6.83 (2H, s, vinyl), 6.72 (1H, s, NH), 5.30 (1H, s, OH), 5.12 (2H, s, CH_2), 1.45 (18H, s, CH_3); IR ($CDCl_3$, cm^{-1}) 3627, 3335, 2958, 1713. Anal. Calcd for $C_{26}H_{30}N_2O_5$: C, 69.31; H, 6.71; N, 6.22. Found: C, 69.51; H, 6.53; N, 5.97.

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propanoyl chloride 7.[8] To a cooled solution of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoic acid (1 g, 3.6 mmol) in chloroform (10 mL) in an ice bath was added dropwise thionyl chloride (0.86 g, 7.2 mmol). The reaction mixture was refluxed for 6 h and evaporated to give the crude product, which was used without further purification for next reaction.

Synthesis of Monomeric Antioxidant 8. To a solution of *N*-(4-hydroxyphenyl) maleimide 6 [7] (1 g, 5.29 mmol) in dry THF (20 mL) was added a solution of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoyl chloride **7** (1.57 g, 5.29 mmol) in THF (30 mL) and triethylamine (0.8 mL, 5.81 mmol) in an ice bath. The reaction mixture was stirred for 2 h in an ice bath, poured into water, extracted with ether, dried, filtered, and evaporated. The crude product was purified by flash column chromatography to give the desired monomeric antioxidant in 60% yield. R_f = 0.5 (ethyl acetate/hexane, 3 : 7); mp 137-140 °C; ^{1}H NMR ($CDCl_3$) 7.36 (2H, d, Ar), 7.12 (2H, d, Ar), 7.06 (2H, s, Ar), 6.76 (2H, s, vinyl), 5.14 (1H, s, OH), 3.02 (2H, t, CH_2), 2.89 (2H, t, CH_2), 1.44 (18H, s, CH_3); IR ($CDCl_3$, cm^{-1}) 3630, 2957, 1756, 1718. Anal. Calcd for $C_{27}H_{31}NO_5$: C, 72.14; H, 6.95; N, 3.12. Found: C, 72.75; H, 6.68; N, 2.87.

Radical Polymerization of Monomeric Antioxidants. A representative radical polymerization procedure was as follows: A mixture of monomeric antioxidant **5** (1 g, 2.2 mmol) and AIBN (4.5 mg, 0.027 mmol) was dissolved in benzene (5 mL) and heated to reflux under nitrogen for 24 h. A polymer formed was dissolved in DCM and poured into hexane. The precipitated polymer was collected. Then this procedure was carried out more two times. The precipitate was dried under vacuum to give the polymer of 0.95 g (95% yield). η_{inh}=0.30 dL/g (c, 0.43 g/dL in THF at 26 °C). ^{1}H NMR ($CDCl_3$) 7.30-6.50 (6H, br, Ar), 5.40-5.00 (3H, br, OH + CH_2), 4.20-3.70 (2H, br, CH), 1.60-1.20 (18H, br, CH_3); IR ($CDCl_3$, cm^{-1}) 3637, 3324, 2957, 1706.

Results and Discussion

Synthesis of Monomeric Antioxidants. Monomeric antioxidants **3**, **5**, and **8** were prepared as shown in Scheme 1. 3,5-Di-*tert*-butyl-4-hydroxybenzyl alcohol **1** and *N*-[4-(chlorocarbonyl)phenyl]maleimide **2** were prepared according to the known procedure.[6,7] Monomeric antioxidant **3** was prepared by the reaction of benzyl alcohol **1** with maleimide **2** in the presence of imidazole in 60% yield. The hydroxy group (-OH) of **1** and acyl chloride (-COCl) of **2** were combined to form ester. The structure was confirmed by proton-NMR, IR spectra, and elemental analysis. The stretching peak of the carbonyl group of **3** appeared at 1716 cm^{-1}. Monomeric antioxidant **5** was also synthesized from the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol **1** and maleimide **4** in reflux in 80% yield. The isocyanate group (-NCO), reaction intermediate of **4**, and hydroxy group (-OH) of **1** reacted to form carbamate. From the literature procedure, acyl chloride **2** in DCM was reacted with sodium azide in water.[9] This reaction occurred at the interface of an aqueous and an organic layer without the whole disappearance of **2**. Thus, a phase transfer catalyst, triethylamine HCl salt was added to the reaction mixture to improve the yield to 95%. The stretching peak of the carbonyl group of **5** appeared at 1713 cm^{-1}. Antioxidant **8** was prepared by the reaction of *N*-(4-hydroxyphenyl)maleimide **6** and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic chloride **7** in the presence of triethylamine in 60% yield, showing the strong stretching carbonyl bands in 1756 and 1718 cm^{-1}. Antioxidant **8** bearing a 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate group will show more thermal stability and lower yellowness. Most commercially available antioxidants contain a 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate group.[1,2] From Table 1, the thermal stability of these new antioxidants was higher than that of a common commercial antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT).[4] However the thermal stability of these monomeric antioxidants was still not high enough to stand the usual polymer thermal

Table 1. Thermal Stability of Monomers and Homopolymers

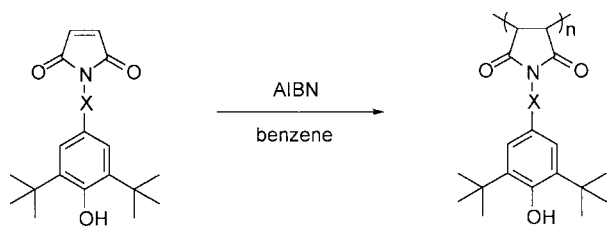
Antioxidant	**3**	**5**	**8**	Polymer of **3**	Polymer of **5**	Polymer of **8**
Degradation temperature (°C)[a]	175	200	275	210	250	350

[a]Onset temperature of mass loss in TGA curves.

Table 2. Free Radical Polymerization of **3**, **5**, and **8** with AIBN in Benzene

Monomer	Monomer/ Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)	Mw[a] ($\times 10^3$)	Mw/Mn	η_{inh}[b] (dL/g)
3	0.46	1.2	24	51	15.4	2.5	0.17
5	0.44	1.2	24	95	46.6	4.6	0.30
8	0.44	1.2	24	89	42.9	4.2	0.25

[a]Measured by GPC in THF with polystyrene standards. [b]Inherent viscosity of polymers with concentration as follows: **3**; 0.37 g/dL. **5**; 0.43 g/dL. and **8**: 0.22 g/dL in THF at 26 °C.



Scheme 2

processing (220-350 °C). Therefore these monomeric antioxidants were not suitable for the application as antioxidant but they could be used for preparing polymeric antioxidants[3] and polymer-bound antioxidants.[10]

Radical Polymerization of Monomeric Antioxidants 3, 5, and 8. Monomeric antioxidants **3**, **5**, and **8** were polymerized by AIBN to obtain the desired polymer (Scheme 2). Polymerization reactions were performed in benzene solution at 90 °C. The polymerization results are summarized in Table 2. Proton NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the required polymer structures. Hindered phenolic antioxidants as free radical scavengers may interfere with the radical initiator, AIBN to form a stable phenoxide radical which is a source of antioxidation. However Munteanu and co-workers reported that the hindered phenolic antioxidants were capable of homopolymerization[5] and grafting onto PE in the presence of free radical initiators.[10d] Recently we also confirmed that a monomeric antioxidant **3** was grafted onto polyethylene by melt processing with free-radical initiators.[11] It is known that hindered phenolic antioxidants trap the peroxy radicals (ROO·) rather than the alkyl radicals (R·) in the stabilization mechanism.[12] Thus our monomeric antioxidants **3**, **5**, and **8** were, as expected, homopolymerized in the presence of free-radicals. The polymers were soluble in chloroform, acetone, ethyl acetate, THF, and DCM. The inherent viscosity, measured in THF at 25 °C was in the range of 0.17-0.30 dL/g. The thermal behaviour of the homopolymers was investigated by thermogravimetric analysis (TGA) to determine the thermal stability. The resulting polymers showed the thermal stability in the range of 210-350 °C as shown in Table 1. The polymer of **8** showed the highest thermal stability up to 350 °C enough to perform the usual polymer processing. The thermal antioxidative effect by aging test and the resistance to extraction by some solvents in the polyolefins matrix are in progress and the full account of the work will be reported in due course.

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